

# A UB3LYP and UMP2 theoretical investigation on unusual cation– $\pi$ interaction between the triplet state HB=BH ( $^3\Sigma_g^-$ ) and $H^+$ , $Li^+$ , $Na^+$ , $Be^{2+}$ or $Mg^{2+}$

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**Abstract** The nature of the unusual cation– $\pi$  interactions between cations ( $H^+$ ,  $Li^+$ ,  $Na^+$ ,  $Be^{2+}$  and  $Mg^{2+}$ ) and the electron-deficient B=B bond of the triplet state HB=BH ( $^3\Sigma_g^-$ ) was investigated using UMP2(full) and UB3LYP methods at 6–311++G(2df,2p) and aug-cc-pVTZ levels, accompanied by a comparison with 1:1 and 2:1  $\sigma$ -binding complexes between BH and the cations. The binding energies follow the order HB=BH... $H^+$  > HB=BH... $Be^{2+}$  > HB=BH... $Mg^{2+}$   $\gg$  HB=BH... $Li^+$  > HB=BH... $Na^+$  and HB=BH ( $^1\Delta_g$ )... $M^+/M^{2+}$  >  $H_2C=CH_2$ ... $M^+/M^{2+}$  >  $HC\equiv CH$ ... $M^+/M^{2+}$  > HB=BH ( $^3\Sigma_g^-$ )... $M^+/M^{2+}$ . Furthermore, except for HB... $H^+$ , the  $\sigma$ -binding interaction energy of the 1:1 complex HB... $M^+/M^{2+}$  is stronger than the cation– $\pi$

interaction energy of the  $C_2H_2$ ... $M^+/M^{2+}$ ,  $C_2H_4$ ... $M^+/M^{2+}$ ,  $B_2H_2$  ( $^1\Delta_g$ )... $M^+/M^{2+}$  or  $B_2H_2$  ( $^3\Sigma_g^-$ )... $M^+/M^{2+}$  complex, and, for the 2:1  $\sigma$ -binding complexes, except for  $HBBBe^{2+}$ ...BH, they are less stable than the cation– $\pi$  complexes of  $B_2H_2$  ( $^1\Delta_g$ ) or  $B_2H_2$  ( $^3\Sigma_g^-$ ). The atoms in molecules (AIM) theory was also applied to verify covalent interactions in the  $H^+$  complexes and confirm that HB=BH ( $^3\Sigma_g^-$ ) can be a weaker  $\pi$ -electron donor than HB=BH ( $^1\Delta_g$ ),  $H_2C=CH_2$  or  $HC\equiv CH$  in the cation– $\pi$  interaction. Analyses of natural bond orbital (NBO) and electron density shifts revealed that the origin of the cation– $\pi$  interaction is mainly that many of the lost densities from the  $\pi$ -orbital of B=B and CC multiple bonds are shifted toward the cations.

**Keywords** B=B double bond · Cation– $\pi$  interaction · Electron density shifts

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## Introduction

Recently, due to their extremely important roles in a wide range of biological and chemical fields (including enzyme–substrate recognition, catalyst development, new drugs and nanomaterial design), cation– $\pi$  interactions have received much attention in experimental studies and theoretical calculations [1–26]. It has been shown that, due to the strong fluidity of the  $\pi$ -electrons of the electron-rich species, cation– $\pi$  interactions can be established between electron-rich multiple bonds such as double bonds, triple bonds, aromatic and cyclooctatetraene rings and their derivatives as  $\pi$ -electron donors, and cations ( $H^+$ ,  $NH_4^+$  and the alkali-metal, alkaline earth-metal, transition-metal cations, etc.) [1–26]. Very interestingly, we have recently investigated cation– $\pi$  interactions between cations ( $H^+$ ,  $Li^+$ ,

$\text{Na}^+$ ,  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$ ) and the singlet state  $\text{HB}=\text{BH}$  ( $^1\Delta_g$ ) or  $\text{HC}\equiv\text{CH}$ , confirming that  $\text{HB}=\text{BH}$  ( $^1\Delta_g$ ) can form stronger cation– $\pi$  interactions than  $\text{HC}\equiv\text{CH}$  [1]. This result has suggested that  $\pi$ -electrons prefer to be released from the electron-deficient  $\text{B}=\text{B}$  double bond, and that the electron-deficient  $\text{B}=\text{B}$  double bond might also act as a  $\pi$ -electron donor to form cation– $\pi$  interactions. Then, since the electron-deficient  $\text{B}=\text{B}$  bond of  $\text{HB}=\text{BH}$  ( $^3\Sigma_g^-$ ) is weaker than that of  $\text{HB}=\text{BH}$  ( $^1\Delta_g$ ) [27], can it act as a  $\pi$ -electron donor to form cation– $\pi$  interactions? However, to our knowledge, no investigation on the cation– $\pi$  interaction involving the  $\text{B}=\text{B}$  bond of  $\text{HB}=\text{BH}$  ( $^3\Sigma_g^-$ ) as  $\pi$ -electron donor has been presented.

For a long time,  $\text{HB}=\text{BH}$  ( $^3\Sigma_g^-$ ) has been of great chemical interest in exploring the nature of the electron-deficient  $\text{B}=\text{B}$  double-bond [27–36]. Knight et al. [27] reported the first definitive experimental characterization and carried out the CI calculations. They found that the valence molecular orbitals of  $\text{HB}=\text{BH}$  ( $^3\Sigma_g^-$ ) were  $(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2$  and  $(1\pi_u)^2$ , where the two unpaired electrons occupy degenerate boron  $2p_x$  and  $2p_y$  bonding orbitals, indicating that it could be described as acetylene with one electron removed from each of the  $\pi$  type orbitals [27]. This suggests that, akin to acetylene, the electron-deficient  $\text{B}_2\text{H}_2$  ( $^3\Sigma_g^-$ ) might offer  $\pi$ -electrons the possibility to form cation– $\pi$  interactions with  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$ .

In this work, our goal was to test the unusual cation– $\pi$  interaction between the electron-deficient  $\text{B}=\text{B}$  double bond of the triplet state  $\text{HB}=\text{BH}$  ( $^3\Sigma_g^-$ ) and  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Be}^{2+}$  or  $\text{Mg}^{2+}$ . For this type of novel cation– $\pi$  interaction, theoretical investigation will first be used to reveal the nature of the interaction in order to allow further theoretical and experimental study of the structures and activities of complexes involving electron-deficient species as  $\pi$ -electron donors.

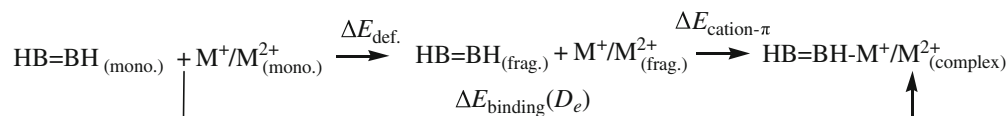
As a new and unusual  $\pi$ -electron donor for cation– $\pi$  interactions, it is essential to compare the  $\text{B}=\text{B}$  bond with the conventional  $\pi$ -electron donor CC multiple bond. First, since the electron structure of  $\text{B}_2\text{H}_2$  ( $^3\Sigma_g^-$ ) resembles that of  $\text{C}_2\text{H}_2$  [27, 36], it becomes possible to adequately describe the properties of these cation– $\pi$  complexes with  $\text{B}_2\text{H}_2$  ( $^3\Sigma_g^-$ ) and to explore the nature of the cation– $\pi$  interaction. Secondly, the greater the flow of  $\pi$ -electrons, the stronger the cation– $\pi$  interaction becomes. In general, due to the nature of the electron-deficient  $\text{B}=\text{B}$  bond, fluidity of the  $\pi$ -electrons is weaker for the  $\text{B}=\text{B}$  bond than for the CC multiple bond, resulting in poorer cation– $\pi$  interactions in

complexes involving the  $\text{B}=\text{B}$  bonds. However, the electron is released more easily from the boron atom than from the carbon atom due to the metallicity of the boron atom, perhaps leading to the stronger cation– $\pi$  interaction observed. Thus the question arises, is the  $\text{B}=\text{B}$  bond of  $\text{B}_2\text{H}_2$  ( $^3\Sigma_g^-$ ) a weaker or stronger  $\pi$ -electron donor for the cation– $\pi$  interaction than the CC multiple bonds?

## Computational methods

It is well established that high-level quantum chemical calculations with electron correlations and a large basis set including both diffuse and polarization functions are crucial to adequately describe the properties of these complexes [37–40]. Furthermore, the augmented correlation-consistent polarized valence-triple- $\zeta$  (aug-cc-pVTZ) basis set has been successfully applied in order to understand the nature of intermolecular interactions as well as changes in the structural, electronic and vibrational properties after molecular complexation [37–40]. On the other hand, the isolated  $\text{HB}=\text{BH}$  monomer has an open-shell ground electronic state ( $^3\Sigma_g^-$ ) so we decided to use the DFT-UB3LYP and UMP2 (full) methods with 6–311++G(2df,2p) and aug-cc-pVTZ atomic basis sets for the monomer and complexes of  $\text{HB}=\text{BH}$  ( $^3\Sigma_g^-$ ) in this investigation. The B3LYP and MP2 (full) methods were employed only with  $\text{HB}=\text{BH}$  ( $^1\Delta_g$ ),  $\text{HC}\equiv\text{CH}$  or  $\text{H}_2\text{C}=\text{CH}_2$ .

All calculations were performed using Gaussian 03 programs [41]. All possible cation– $\pi$  interaction complexes were fully optimized using (U)MP2(full) and (U)B3LYP methods with the 6-311++G(2df,2p) and aug-cc-pVTZ basis sets. The complexes with  $\text{H}^+$ ,  $\text{Li}^+$  and  $\text{Na}^+$  corresponding to the minimum energy points—at which the harmonic frequency analyses were carried out and the complexes have no imaginary frequency—at the molecular energy hypersurface were obtained. In contrast, the  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$  complexes with  $\text{HB}=\text{BH}$  ( $^1\Delta_g$ ),  $\text{HB}=\text{BH}$  ( $^3\Sigma_g^-$ ),  $\text{H}_2\text{C}=\text{CH}_2$  and  $\text{HC}\equiv\text{CH}$  are not true minima, and vibrational analysis gives one imaginary frequency for each complex. Natural bonding analysis [42] was also carried out at (U)MP2(full)/aug-cc-pVTZ. The shifts in electron density [43] that accompany formation of cation– $\pi$  interactions were displayed at (U)MP2(full)/aug-cc-pVTZ level using the program GaussView, and the topological electron charge densities were analyzed by the atoms in molecules (AIM) method [44] using the program AIMPAC [45] at the same level. The frequency shifts ( $\Delta\nu$ ), defined as the difference between



the frequency of the certain vibrational mode in the complex and in the isolated  $B_2H_2$ , can be expressed as follows:

$$\Delta\nu = \nu_{\text{complex}} - \nu_{\text{monomer}} \quad (1)$$

Binding energy ( $D_e$ ) is defined as:

Because the deformation energy ( $\Delta E_{\text{def}}$ ), defined as the energy difference between the isolated molecule and the molecular framework at the geometry of the complex, is often negligible [37–40], the value of cation– $\pi$  interaction energy ( $\Delta E_{\text{cation}-\pi}$ ) is almost equal to that of the binding energy ( $D_e$ ). So, for these systems, it can be expressed as follows:

$$D_e = E_{(\text{HB}=\text{BH}-\text{M}^+/\text{M}^{2+})_{\text{complex}}} - E_{(\text{HB}=\text{BH})_{\text{mono}}} - E_{(\text{M}^+/\text{M}^{2+})_{\text{mono}}} \quad (2)$$

The  $D_e$  corrected for the basis set superposition error (BSSE) [46, 47] and zero-point energy (ZPE) correction was evaluated.

## Results and discussion

The atomic labels and bond critical points (BCPs) of the complexes are shown in Fig. 1, and the corresponding geometry parameters and binding energies are listed in Tables 1 and 2, respectively. The frequency shifts of  $B_2H_2$  ( ${}^3\Sigma_g^-$ ) in complexes are presented in Table 3. The natural bond orbital (NBO) analysis and the electron densities at the BCPs are given in Tables 4 and 5, respectively. The plot of binding energies versus  $\rho_{\text{BCP}(\text{cation}\cdots\pi)}$  and the shifts of electron densities are illustrated in Figs. 2 and 3, respec-

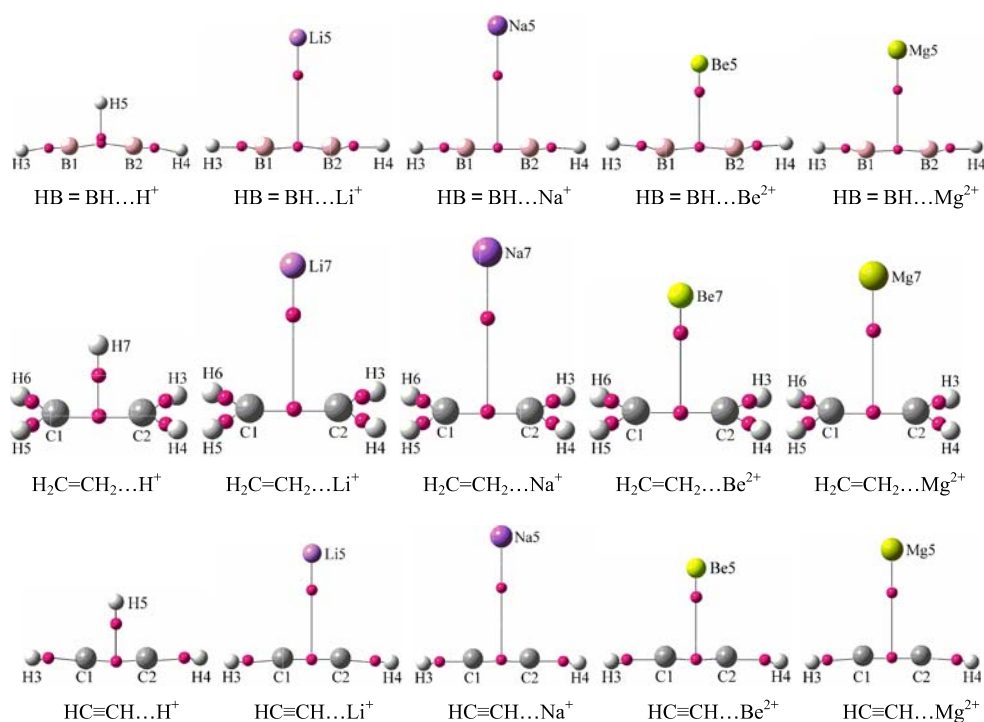
tively. The results reveal that the nature of the cation– $\pi$  interaction between  $\text{HB}=\text{BH}$  ( ${}^3\Sigma_g^-$ ) and  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Be}^{2+}$  or  $\text{Mg}^{2+}$  is that many of the lost densities from the  $\pi$ -orbital of  $\text{B}=\text{B}$  and  $\text{C}=\text{C}$  multiple bonds are shifted toward the cations, and  $\text{HB}=\text{BH}$  ( ${}^3\Sigma_g^-$ ) acts as a weaker  $\pi$ -electron donor of the cation– $\pi$  interaction than  $\text{HB}=\text{BH}$  ( ${}^1\Delta_g$ ),  $\text{HC}\equiv\text{CH}$  or  $\text{H}_2\text{C}=\text{CH}_2$ . Furthermore, all the complexes of  $\text{H}^+$  are indicative of covalent interactions.

### Geometry of the complex

As can be seen from Fig. 1, all the cation– $\pi$  complexes form the  $C_{2v}$  T-shape with the cations lying perpendicular to the  $\text{B}=\text{B}$  or  $\text{C}=\text{C}$  multiple bonds and pointing toward to their midpoints.  $\text{HB}=\text{BH}$  ( ${}^3\Sigma_g^-$ )... $\text{M}^+/\text{M}^{2+}$  is of electronic state  ${}^3B_1$ , whereas the others are the  ${}^1A_1$  electronic states.

From Table 1, for  $\text{HB}=\text{BH}$  ( ${}^3\Sigma_g^-$ )... $\text{H}^+$ , the increment of the  $\text{B}=\text{B}$  bond length is increased by 0.074 Å, i.e., higher than those of the  $\text{C}=\text{C}$  multiple bonds in  $\text{HC}\equiv\text{CH}$ ... $\text{H}^+$  and  $\text{H}_2\text{C}=\text{CH}_2$ ... $\text{H}^+$  by 58.0 and 27.0 mÅ at (U)MP2(full)/aug-cc-PVTZ level, respectively. It is also larger than that of the  $\text{B}=\text{B}$  bond length in  $\text{HB}=\text{BH}$  ( ${}^1\Delta_g$ )... $\text{H}^+$  by 30.0 mÅ at the same level. Furthermore, the distance of the  $\text{H}^+\cdots\pi$  bond in  $\text{HB}=\text{BH}$  ( ${}^3\Sigma_g^-$ )... $\text{H}^+$  is 1.068 Å, whereas the corresponding values in  $\text{HC}\equiv\text{CH}$ ... $\text{H}^+$ ,  $\text{H}_2\text{C}=\text{CH}_2$ ... $\text{H}^+$  and  $\text{HB}=\text{BH}$  ( ${}^1\Delta_g$ )... $\text{H}^+$  are 1.112, 1.107 and 1.187 Å, i.e., lower than those in the complexes of  $\text{HC}\equiv\text{CH}$ ,  $\text{H}_2\text{C}=\text{CH}_2$  and  $\text{HB}=\text{BH}$  ( ${}^1\Delta_g$ ) by 0.044, 0.039 and 0.119 Å at (U)MP2(full)/aug-cc-PVTZ level, respectively. Thus, a cation– $\pi$  interaction in  $\text{HB}=\text{BH}$  ( ${}^3\Sigma_g^-$ )... $\text{H}^+$  is suggested.

**Fig. 1** Molecular structures and bond critical points (BCPs) of the cation– $\pi$  complexes



**Table 1** Principal geometry parameters (in Å) for HB=BH ( $^3\Sigma_g^-$ ), HB=BH ( $^1\Delta_g$ ), H<sub>2</sub>C=CH<sub>2</sub>, HC≡CH and their complexes

	HB=BH( $^3\Sigma_g^-$ )	HB=BH( $^3\Sigma_g^-$ )...H <sup>+</sup>	HB=BH( $^3\Sigma_g^-$ )...Li <sup>+</sup>	HB=BH( $^3\Sigma_g^-$ )...Na <sup>+</sup>	HB=BH( $^3\Sigma_g^-$ )...Be <sup>2+</sup>	HB=BH( $^3\Sigma_g^-$ )...Mg <sup>2+</sup>
R(M <sup>+</sup> /M <sup>2+</sup> ...π)		1.087 <sup>a</sup> 1.087 <sup>b</sup>	2.475 2.471	2.878 2.878	1.906 1.906	2.763 2.763
		1.073 <sup>c</sup> 1.068 <sup>d</sup>	2.492 2.459	2.900 2.871	1.914 1.894	2.498 2.444
R(B1=B2)	1.506 <sup>a</sup> 1.506 <sup>b</sup>	1.586 1.586	1.519 1.519	1.516 1.516	1.589 1.589	1.569 1.569
	1.505 <sup>c</sup> 1.499 <sup>d</sup>	1.579 1.573	1.518 1.512	1.515 1.508	1.587 1.577	1.557 1.547
	HB=BH( $^1\Delta_g$ )	HB=BH( $^1\Delta_g$ )...H <sup>+</sup>	HB=BH( $^1\Delta_g$ )...Li <sup>+</sup>	HB=BH( $^1\Delta_g$ )...Na <sup>+</sup>	HB=BH( $^1\Delta_g$ )...Be <sup>2+</sup>	HB=BH( $^1\Delta_g$ )...Mg <sup>2+</sup>
R(M <sup>+</sup> /M <sup>2+</sup> ...π) <sup>c</sup>		1.199 <sup>a</sup> 1.201 <sup>b</sup>	2.486 2.479	2.836 2.836	2.241 2.241	2.634 2.634
		1.187 <sup>c</sup> 1.187 <sup>d</sup>	2.486 2.466	2.855 2.839	2.212 2.176	2.590 2.556
R(B1=B2) <sup>c</sup>	1.520 <sup>a</sup> 1.520 <sup>b</sup>	1.565 1.565	1.534 1.534	1.534 1.534	1.608 1.608	1.590 1.590
	1.524 <sup>c</sup> 1.518 <sup>d</sup>	1.565 1.558	1.538 1.530	1.537 1.529	1.608 1.596	1.585 1.575
	H <sub>2</sub> C=CH <sub>2</sub>	H <sub>2</sub> C=CH <sub>2</sub> ...H <sup>+</sup>	H <sub>2</sub> C=CH <sub>2</sub> ...Li <sup>+</sup>	H <sub>2</sub> C=CH <sub>2</sub> ...Na <sup>+</sup>	HC=CH...Be <sup>2+</sup>	HC=CH...Mg <sup>2+</sup>
R(M <sup>+</sup> /M <sup>2+</sup> ...π)		1.125 <sup>a</sup> 1.125 <sup>b</sup>	2.266 2.266	2.646 2.644	1.869 1.869	2.304 2.303
		1.108 <sup>c</sup> 1.107 <sup>d</sup>	2.264 2.239	2.645 2.625	1.857 1.841	2.256 2.256
R(C1=C2)	1.325 <sup>a</sup> 1.325 <sup>b</sup>	1.376 1.376	1.337 1.337	1.335 1.335	1.382 1.381	1.368 1.368
	1.329 <sup>c</sup> 1.328 <sup>d</sup>	1.376 1.375	1.340 1.339	1.338 1.336	1.379 1.377	1.364 1.363
	HC≡CH	HC≡CH...H <sup>+</sup>	HC≡CH...Li <sup>+</sup>	HC≡CH...Na <sup>+</sup>	HC≡CH...Be <sup>2+</sup>	HC≡CH...Mg <sup>2+</sup>
R(M <sup>+</sup> /M <sup>2+</sup> ...π)		1.134 <sup>a</sup> 1.134 <sup>b</sup>	2.213 2.213	2.610 2.612	1.787 1.789	2.256 2.256
		1.115 <sup>c</sup> 1.112 <sup>d</sup>	2.211 2.197	2.610 2.610	1.784 1.774	2.243 2.224
R(C1=C2)	1.196 <sup>a</sup> 1.196 <sup>b</sup>	1.217 1.217	1.202 1.202	1.200 1.200	1.223 1.223	1.216 1.216
	1.208 <sup>c</sup> 1.208 <sup>d</sup>	1.225 1.224	1.213 1.214	1.212 1.212	1.232 1.231	1.225 1.224

<sup>a</sup> At (U)B3LYP/6–311++G(2df,2p) level<sup>b</sup> At (U)B3LYP/aug-cc-PVTZ level<sup>c</sup> At (U)MP2(full)/6–311++G(2df,2p) level<sup>d</sup> At (U)MP2(full)/aug-cc-PVTZ level<sup>e</sup> Calculated values from Ref. [1]

Similar to HB=BH ( $^3\Sigma_g^-$ )...H<sup>+</sup>, the cation–π interaction is also found in HB=BH ( $^3\Sigma_g^-$ )...Li<sup>+</sup> or HB=BH ( $^3\Sigma_g^-$ )...Na<sup>+</sup>, according to the higher increments of the B=B bond lengths and the larger slightly M<sup>+</sup>...π bond distances than in HC≡CH/H<sub>2</sub>C=CH<sub>2</sub>...Li<sup>+</sup> or HC≡CH/H<sub>2</sub>C=CH<sub>2</sub>...Na<sup>+</sup>. The increments of the B=B bond lengths are increased by 0.013 and 0.009 Å in HB=BH ( $^3\Sigma_g^-$ )...Li<sup>+</sup> and HB=BH ( $^3\Sigma_g^-$ )...Na<sup>+</sup>, whereas the corresponding values of the C≡C bond distances in HC≡CH...Li<sup>+</sup>/Na<sup>+</sup> are both elongated by 0.004 Å, and those of the C=C bond distances are 0.011 and 0.008 Å at (U)MP2(full)/aug-cc-PVTZ level, respectively. Furthermore, the increment of the B=B bond length in HB=BH ( $^3\Sigma_g^-$ )...Li<sup>+</sup>/Na<sup>+</sup> is close to that in HB=BH ( $^1\Delta_g$ )...Li<sup>+</sup> (0.012 Å) and HB=BH ( $^1\Delta_g$ )...Na<sup>+</sup> (0.011 Å). In HB=BH ( $^3\Sigma_g^-$ )...Li<sup>+</sup> and HB=BH ( $^3\Sigma_g^-$ )...Na<sup>+</sup>, M<sup>+</sup>...π bond distances are 2.459 and 2.871 Å, respectively, while for the complexes of HC≡CH, H<sub>2</sub>C=CH<sub>2</sub> and HB=BH ( $^1\Delta_g$ ), Li<sup>+</sup>...π bond distances are 2.197, 2.239 and 2.466 Å, and Na<sup>+</sup>...π bond lengths are up to 2.610, 2.625 and 2.839 Å with the (U)MP2(full)/aug-cc-PVTZ method, respectively.

Cation–π interactions are also observed in both HB=BH ( $^3\Sigma_g^-$ )...Be<sup>2+</sup> and HB=BH ( $^3\Sigma_g^-$ )...Mg<sup>2+</sup> (Table 1 and

Fig. 1). The distance of the B=B bond is lengthened from 1.499 to 1.577 and 1.547 Å in HB=BH ( $^3\Sigma_g^-$ )...Be<sup>2+</sup> and HB=BH ( $^3\Sigma_g^-$ )...Mg<sup>2+</sup> at UMP2(full)/aug-cc-PVTZ level, respectively. However, it is changed only from 1.208 to 1.231 and 1.224 Å in the HC≡CH complexes, from 1.328 to 1.377 and 1.363 Å in the complexes of H<sub>2</sub>C=CH<sub>2</sub>, and from 1.518 to 1.596 and 1.575 Å in HB=BH ( $^1\Delta_g$ )...Be<sup>2+</sup> and HB=BH ( $^1\Delta_g$ )...Mg<sup>2+</sup>, respectively. Furthermore, the distance of the M<sup>2+</sup>...π bond in HB=BH ( $^3\Sigma_g^-$ )...Be<sup>2+</sup> or HB=BH ( $^3\Sigma_g^-$ )...Mg<sup>2+</sup>, up to 1.894 or 2.444 Å, is close to those in the complexes of HC≡CH (1.774 and 2.224 Å) or H<sub>2</sub>C=CH<sub>2</sub> (1.841 and 2.256 Å) at (U)MP2(full)/aug-cc-PVTZ level, respectively. Moreover, the distance of the M<sup>2+</sup>...π bond in HB=BH ( $^3\Sigma_g^-$ )...Be<sup>2+</sup> or HB=BH ( $^3\Sigma_g^-$ )...Mg<sup>2+</sup> is lower than that in HB=BH ( $^1\Delta_g$ )...Be<sup>2+</sup> (2.176 Å) or HB=BH ( $^1\Delta_g$ )...Mg<sup>2+</sup> (2.556 Å).

As can be seen from Table 1, the distance of the cation–π bond follows the same order of Na<sup>+</sup>...π > Li<sup>+</sup>...π or Mg<sup>2+</sup>...π > Be<sup>2+</sup>...π at four levels for each of the complexes, and the increments of the B=B, C≡C or C=C bond length follow the same order in Na<sup>+</sup>...π < Li<sup>+</sup>...π or Mg<sup>2+</sup>...π < Be<sup>2+</sup>...π complexes. These results suggest that the strength of the

**Table 2** Binding energies of the cation- $\pi$  complexes [ $-D_e$  (kJ mol $^{-1}$ )]

	HB=BH( $^3\Sigma_g^-$ )...H $^+$	HB=BH( $^3\Sigma_g^-$ )...Li $^+$	HB=BH( $^3\Sigma_g^-$ )...Na $^+$	HB=BH( $^3\Sigma_g^-$ )...Be $^{2+}$	HB=BH( $^3\Sigma_g^-$ )...Mg $^{2+}$
UMp2(full)/6-311++G**	623.46 (617.01) <sup>a</sup>	51.76 (48.51)	30.73 (27.67)	497.58 (491.47)	243.25 (238.99)
UMp2(full)/6-311++G(2df,2p)	620.81 (617.35) <sup>a</sup> 597.48 <sup>b</sup>	53.74 (51.39) 49.59	35.15 (32.80) 31.74	497.45 (493.09) 493.90	248.94 (245.50) 245.67
UMP2(full)/aug-cc-pVTZ	624.25 (617.59) 598.50	58.04 (52.10) 50.54	40.88 (31.13) 29.76	513.87 (491.76) 493.40	261.23 (245.68) 246.10
UB3LYP/6-311++G(2df,2p)	620.54	57.07 (56.33) 54.53	37.67 (36.14) 35.00	530.84 (530.21) 531.45	284.46 (283.49) 284.06
UB3LYP/aug-cc-pVTZ	621.19	58.02 (57.43) 55.65	37.40 (37.07) 35.93	532.53 (531.78) 533.05	287.02 (286.42) 287.02
	HB=BH( $^1\Delta_g$ )...H $^+$	HB=BH( $^1\Delta_g$ )...Li $^+$	HB=BH( $^1\Delta_g$ )...Na $^+$	HB=BH( $^1\Delta_g$ )...Be $^{2+}$	HB=BH( $^1\Delta_g$ )...Mg $^{2+}$
MP2(full)/6-311++G** <sup>c</sup>	857.88 (852.87) <sup>a</sup>	116.39 (111.78)	78.88 (74.64)	723.21 (716.60)	411.32 (405.84)
MP2(full)/6-311++G(2df,2p) <sup>c</sup>	851.12 (848.43) <sup>a</sup> 832.31 <sup>b</sup>	115.63 (112.43) 109.23	81.78 (77.26) 75.16	714.92 (710.37) 707.92	410.40 (406.32) 404.68
MP2(full)/aug-cc-pVTZ <sup>c</sup>	854.36 (849.32) 834.26	119.15 (112.88) 110.07	86.11 (75.84) 73.54	725.61 (708.08) 706.13	419.61 (405.45) 404.20
B3LYP/6-311++G(2df,2p) <sup>c</sup>	849.65	120.34 (119.55) 116.51	88.08 (86.43) 84.35	744.54 (743.97) 742.09	453.35 (452.11) 450.81
B3LYP/aug-cc-pVTZ <sup>c</sup>	849.82	120.97 (120.43) 117.49	87.33 (87.04) 85.05	745.85 (745.26) 743.57	455.02 (454.67) 453.51
	H $_2$ C=CH $_2$ ...H $^+$	H $_2$ C=CH $_2$ ...Li $^+$	H $_2$ C=CH $_2$ ...Na $^+$	H $_2$ C=CH $_2$ ...Be $^{2+}$	H $_2$ C=CH $_2$ ...Mg $^{2+}$
Mp2(full)/6-311++G**	702.93 (693.75) <sup>a</sup>	88.39 (82.11)	57.01 (51.54)	565.63 (554.78)	295.77 (287.59)
Mp2(full)/6-311++G(2df,2p)	694.97 (690.13) <sup>a</sup> 662.44 <sup>b</sup>	88.90 (84.72) 79.86	60.71 (55.21) 51.63	564.02 (557.69) 554.73	302.38 (296.71) 293.03
MP2(full)/aug-cc-pVTZ	701.00 (691.88) 663.74	94.51 (86.28) 81.36	66.56 (54.65) 52.27	585.70 (559.71) 556.94	319.65 (299.32) 295.97
B3LYP/6-311++G(2df,2p)	703.40	91.76 (90.96) 86.34	62.45 (60.64) 57.17	593.42 (591.61) 589.19	331.48 (330.17) 327.17
B3LYP/aug-cc-pVTZ	704.97	93.25 (92.59) 87.92	62.22 (61.81) 58.25	596.43 (595.54) 593.12	334.86 (334.34) 331.33
	HC≡CH...H $^+$	HC≡CH...Li $^+$	HC≡CH...Na $^+$	HC≡CH...Be $^{2+}$	HC≡CH...Mg $^{2+}$
Mp2(full)/6-311++G** <sup>c</sup>	652.92 (642.39) <sup>a</sup>	87.94 (80.26)	55.60 (49.09)	542.79 (530.34)	273.14 (263.69)
Mp2(full)/6-311++G(2df,2p) <sup>c</sup>	646.95 (641.79) <sup>a</sup> 619.93 <sup>b</sup>	87.43 (83.04) 79.53	58.42 (53.11) 50.93	541.08 (534.22) 531.78	280.75 (274.87) 272.83
MP2(full)/aug-cc-pVTZ <sup>c</sup>	653.11 (643.73) 621.98	91.64 (84.49) 81.34	63.51 (52.60) 50.39	561.41 (535.74) 533.78	295.98 (277.32) 275.44
B3LYP/6-311++G(2df,2p) <sup>c</sup>	661.88	91.83 (91.00) 87.67	60.88 (59.25) 57.17	573.98 (573.20) 572.76	308.77 (307.48) 306.37
B3LYP/aug-cc-pVTZ <sup>c</sup>	663.53	93.27 (92.62) 89.37	60.55 (60.15) 58.15	576.82 (575.89) 575.66	312.02 (311.51) 310.61

<sup>a</sup> The value in parenthesis is basis set superposition error (BSSE)-corrected [ $-D_{e(BSSE)}$ ]

<sup>b</sup> The binding energy is  $\Delta E$  with BSSE and zero-point energy [ZPE;  $-D_{e(BSSE-ZPE)}$ ] correction

<sup>c</sup> Calculated values from Ref. [1]

cation- $\pi$  interaction in Li $^+$  or Be $^{2+}$  complexes might be greater than that in the complex of Na $^+$  or Mg $^{2+}$ . In particular, the H $^+$ ... $\pi$  distances are considerably smaller than the corresponding distances in other complexes, indicating that the cation- $\pi$  interaction might be greatest in the H $^+$  complex.

#### Binding energies and stabilities

For all the complexes, the proportion of correlated interaction energies to their total binding energies, defined as  $[(-D_e)-(-D_{e(BSSE/ZPE)})]/(-D_e)$ , are up to 9.10, 23.85,

**Table 3** Selected frequency shifts relative to HB=BH ( $^3\Sigma_g^-$ ) for the complexes and IR intensities in the complexes at UMP2(full)/aug-cc-pVTZ level<sup>a</sup>. *Stret.* Stretching

	HB=BH		HB=BH...H <sup>+</sup>		HB=BH...Li <sup>+</sup>		HB=BH...Na <sup>+</sup>		HB=BH...Be <sup>2+</sup>		HB=BH...Mg <sup>2+</sup>		Assignment <sup>b</sup>
	$\nu$	<i>I</i>	$\Delta\nu$	<i>I</i>	$\Delta\nu$	<i>I</i>	$\Delta\nu$	<i>I</i>	$\Delta\nu$	<i>I</i>	$\Delta\nu$	<i>I</i>	
$\nu_1$	1,307	0	-186	2	-33	7	-24	8	-199	49	-121	76	sym. stret. of B=B
$\nu_2$	2,850	23	39	52	2	0	2	1	-91	151	-31	45	anti-sym. stret. of B-H
$\nu_3$	2,917	0	13	0	-7	0	-8	0	-112	0	-45	1	stret. of B-H

<sup>a</sup> All frequencies ( $\nu$  or  $\Delta\nu$ ) are in cm<sup>-1</sup> and IR intensities (*I*) are in km mol<sup>-1</sup>

4.06 and 1.01 % at (U)MP2(full)/6-311++G(2df,2p), (U)MP2(full)/aug-cc-pVTZ, (U)B3LYP/6-311++G(2df,2p) and (U)B3LYP/aug-cc-pVTZ levels for BSSE corrections, respectively. For the cation- $\pi$  interactions in the complexes of HB=BH ( $^1\Delta_g$ ), the proportions are up to 5.53, 11.93, 1.87 and 0.44 % at MP2(full)/6-311++G(2df,2p), MP2(full)/aug-cc-pVTZ, B3LYP/6-311++G(2df,2p) and B3LYP/aug-cc-pVTZ levels for BSSE corrections, respec-

tively [1]. These results indicate that, for cation- $\pi$  interaction energies, it is unnecessary to check the BSSE corrections except for the (U)MP2(full)/aug-cc-pVTZ calculation, which is in accordance with most recent investigations [3, 37–40]. As with BSSE corrections, ZPE corrections, which amount to only 5.89, 5.20, 5.56 and 5.72 % for the above methods, respectively, might also be negligible. Our investigation on the cation- $\pi$  interactions

**Table 4** Calculated parameters of the cation- $\pi$  complexes at their equilibrium geometries: natural bond orbital (NBO) occupation numbers, their respective orbital energies  $\varepsilon$ , the second-order perturbation energies  $E^{(2)}$  and the sums of all atomic NBO charges in their complexes (Q) at (U)MP2(full)/aug-cc-pVTZ level

	HB=BH( $^3\Sigma_g^-$ )...Li <sup>+</sup>	HB=BH( $^3\Sigma_g^-$ )...Na <sup>+</sup>	HB=BH( $^3\Sigma_g^-$ )...Be <sup>2+</sup>	HB=BH( $^3\Sigma_g^-$ )...Mg <sup>2+</sup>	
Occ.(B=B) <sup>a</sup>	0.9702 p <sup>1.00</sup> p <sup>1.00</sup>	0.9820 p <sup>1.00</sup> p <sup>1.00</sup>	0.7442 p <sup>1.00</sup> p <sup>1.00</sup>	0.7604 p <sup>1.00</sup> p <sup>1.00</sup>	
$\varepsilon\{(B=B)\}^b$	-0.5601	-0.5309	-0.7933	-0.7031	
Occ.(M <sup>+</sup> /M <sup>2+</sup> ) <sup>a</sup>	0.0227 sp <sup>0.33</sup>	0.0156 sp <sup>0.17</sup>	0.2527 sp <sup>0.12</sup>	0.2360 sp <sup>0.05</sup>	
$\varepsilon\{(M^+/M^{2+})\}^b$	0.1805	0.1286	-0.4523	-0.4523	
$E_{(B=B)\rightarrow(M^+/M^{2+})}^{(2)c}$	45.79	28.52	684.13	413.22	
Q(HB=BH) <sup>d</sup>	26.5	18.9	342.2	256.8	
	H <sub>2</sub> C=CH <sub>2</sub> ...H <sup>+</sup>	H <sub>2</sub> C=CH <sub>2</sub> ...Li <sup>+</sup>	H <sub>2</sub> C=CH <sub>2</sub> ...Na <sup>+</sup>	H <sub>2</sub> C=CH <sub>2</sub> ...Be <sup>2+</sup>	H <sub>2</sub> C=CH <sub>2</sub> ...Mg <sup>2+</sup>
Occ.(C=C)	1.9969 sp <sup>1.99</sup> sp <sup>1.99</sup>	1.9740 p <sup>1.00</sup> p <sup>1.00</sup>	1.9814 p <sup>1.00</sup> p <sup>1.00</sup>	1.6875 p <sup>1.00</sup> p <sup>1.00</sup>	1.8241 p <sup>1.00</sup> p <sup>1.00</sup>
$\varepsilon\{(C=C)\}^b$	-1.2190	-0.5973	-0.5791	-0.8465	-0.8037
Occ.(M <sup>+</sup> /M <sup>2+</sup> ) <sup>a</sup>	0.6853 sp <sup>0.00</sup>	0.0272 sp <sup>0.16</sup>	0.0188 sp <sup>0.03</sup>	0.3141 sp <sup>0.15</sup>	0.1771 sp <sup>0.05</sup>
$\varepsilon\{(M^+/M^{2+})\}^b$	-0.2489	0.1605	-0.0055	-0.3252	-0.3658
$E_{(C=C)\rightarrow(M^+/M^{2+})}^{(2)c}$	94.10	50.48	23.54	785.13	269.24
Q(H <sub>2</sub> C=CH <sub>2</sub> )	687.2	28.8	19.4	326.1	180.8
	HC≡CH...H <sup>+</sup>	HC≡CH...Li <sup>+</sup>	HC≡CH...Na <sup>+</sup>	HC≡CH...Be <sup>2+</sup>	HC≡CH...Mg <sup>2+</sup>
Occ.(C≡C)	1.9935 sp <sup>1.23</sup> sp <sup>1.23</sup>	1.9843 p <sup>1.00</sup> p <sup>1.00</sup>	1.9909 p <sup>1.00</sup> p <sup>1.00</sup>	1.8361 p <sup>1.00</sup> p <sup>1.00</sup>	1.9014 p <sup>1.00</sup> p <sup>1.00</sup>
$\varepsilon\{(C≡C)\}^b$	-1.3982	-0.6680	-0.6147	-0.9720	-0.8751
Occ.(M <sup>+</sup> /M <sup>2+</sup> ) <sup>a</sup>	0.6306 sp <sup>0.00</sup>	0.0147 sp <sup>0.50</sup>	0.0079 sp <sup>0.11</sup>	0.1678 sp <sup>0.19</sup>	0.1009 sp <sup>0.09</sup>
$\varepsilon\{(M^+/M^{2+})\}^b$	-0.2434	0.3388	0.1443	-0.2156	-0.3291
$E_{(C≡C)\rightarrow(M^+/M^{2+})}^{(2)c}$	95.22	36.13	13.01	439.65	161.43
Q(HC≡CH)	663.0	18.7	9.4	196.1	109.8

<sup>a</sup> Occ.: occupation number

<sup>b</sup> In a.u.

<sup>c</sup> In kJ mol<sup>-1</sup>

<sup>d</sup> In me

**Table 5** The selected bond critical point properties (in a.u.) at (U)MP2(full)/aug-cc-pVTZ level

	HB=BH( $^3\Sigma_g^-$ )	HB=BH( $^3\Sigma_g^-$ )...H <sup>+</sup>	HB=BH( $^3\Sigma_g^-$ )...Li <sup>+</sup>	HB=BH( $^3\Sigma_g^-$ )...Na <sup>+</sup>	HB=BH( $^3\Sigma_g^-$ )...Be <sup>2+</sup>	HB=BH( $^3\Sigma_g^-$ )...Mg <sup>2+</sup>
$\rho_{\text{BCP}}(\text{M}^+/\text{M}^{2+} \dots \pi)$		0.1587	0.0143	0.0100	0.0597	0.0283
$\nabla^2 \rho_{\text{BCP}}(\text{M}^+/\text{M}^{2+} \dots \pi)$		-0.1386	0.0507	0.0375	0.0646	0.0528
$\rho_{\text{BCP}}(\text{B}=\text{B})$	0.2057		0.2018	0.2033	0.1806	0.1955
$\nabla^2 \rho_{\text{BCP}}(\text{B}=\text{B})$	-0.4393		-0.4460	-0.4471	-0.4411	-0.4871
	H <sub>2</sub> C=CH <sub>2</sub>	H <sub>2</sub> C=CH <sub>2</sub> ...H <sup>+</sup>	H <sub>2</sub> C=CH <sub>2</sub> ...Li <sup>+</sup>	H <sub>2</sub> C=CH <sub>2</sub> ...Na <sup>+</sup>	H <sub>2</sub> C=CH <sub>2</sub> ...Be <sup>2+</sup>	H <sub>2</sub> C=CH <sub>2</sub> ...Mg <sup>2+</sup>
$\rho_{\text{BCP}}(\text{M}^+/\text{M}^{2+} \dots \pi)$		0.1980	0.0220	0.0155	0.0739	0.0405
$\nabla^2 \rho_{\text{BCP}}(\text{M}^+/\text{M}^{2+} \dots \pi)$		-0.3000	0.0999	0.0750	0.1144	0.1411
$\rho_{\text{BCP}}(\text{C}=\text{C})$	0.3697	0.3382	0.3628	0.3646	0.3435	0.3517
$\nabla^2 \rho_{\text{BCP}}(\text{C}=\text{C})$	-1.4250	-1.2253	-1.3812	-1.3931	-1.2845	-1.3315
	HC≡CH	HC≡CH...H <sup>+</sup>	HC≡CH...Li <sup>+</sup>	HC≡CH...Na <sup>+</sup>	HC≡CH...Be <sup>2+</sup>	HC≡CH...Mg <sup>2+</sup>
$\rho_{\text{BCP}}(\text{M}^+/\text{M}^{2+} \dots \pi)$		0.2155	0.0229	0.0152	0.0780	0.0409
$\nabla^2 \rho_{\text{BCP}}(\text{M}^+/\text{M}^{2+} \dots \pi)$		-0.3755	0.1176	0.0810	0.2172	0.1740
$\rho_{\text{BCP}}(\text{C}\equiv\text{C})$	0.4185	0.4169	0.4194	0.4195	0.4201	0.4216
$\nabla^2 \rho_{\text{BCP}}(\text{C}\equiv\text{C})$	-1.0871	-1.3483	-1.1734	-1.1577	-1.4315	-1.3460

between HB=BH ( $^1\Delta_g$ ) and cations also indicated that ZPE corrections amounted to only 2.77, 2.67, 2.52 and 2.44 % for the above methods, respectively [1].

As can be seen from Table 2, the binding energies obtained from (U)MP2(full) and (U)B3LYP methods at 6–311++G(2df,2p) and aug-cc-pVTZ levels all follow the same order of HB=BH ( $^3\Sigma_g^-$ )...H<sup>+</sup>>HB=BH ( $^3\Sigma_g^-$ )...Be<sup>2+</sup>>HB=BH ( $^3\Sigma_g^-$ )...Mg<sup>2+</sup>>HB=BH ( $^3\Sigma_g^-$ )...Li<sup>+</sup>>HB=BH ( $^3\Sigma_g^-$ )...Na<sup>+</sup>, which is also in good agreement with the analyses of the geometries, and similar to our investigation on the cation– $\pi$  interaction between HB=BH ( $^1\Delta_g$ ) and cation (H<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, Be<sup>2+</sup> or Mg<sup>2+</sup>) [1].

Mohajeri and Karimi have also studied the cation– $\pi$  interaction energy of the C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>...M<sup>+</sup> (M<sup>+</sup>=H<sup>+</sup>, Li<sup>+</sup> and Na<sup>+</sup>) complex; interaction energy was evaluated to be 642.86, 72.26 and 48.97 kJ mol<sup>-1</sup> for C<sub>2</sub>H<sub>2</sub>...M<sup>+</sup> and 694.21, 82.22 and 51.31 kJ mol<sup>-1</sup> for C<sub>2</sub>H<sub>4</sub>...M<sup>+</sup> after correction for BSSE at MP2/6–311++G\*\* level, respectively [16]. From Table 1, the cation– $\pi$  interaction energies of the HB=BH ( $^1\Delta_g$ )...M<sup>+</sup> complexes are 852.87, 111.78 and 74.64 kJ mol<sup>-1</sup> after BSSE, higher than those of the C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>...M<sup>+</sup> complexes. For comparison, we also obtained corresponding values (after BSSE) of 617.01, 48.51 and 27.67 kJ mol<sup>-1</sup> by employing the UMP2(full)/6–311++G\*\* method for the B<sub>2</sub>H<sub>2</sub>...M<sup>+</sup> complexes. Comparing these results, it can be seen that the cation– $\pi$  interaction energy of B<sub>2</sub>H<sub>2</sub> ( $^3\Sigma_g^-$ )...M<sup>+</sup> is weaker than that of the C<sub>2</sub>H<sub>2</sub>...M<sup>+</sup>, C<sub>2</sub>H<sub>4</sub>...M<sup>+</sup> or B<sub>2</sub>H<sub>2</sub> ( $^1\Delta_g$ )...M<sup>+</sup> complex. For the M<sup>2+</sup> complexes, the cation– $\pi$  interactions of B<sub>2</sub>H<sub>2</sub> ( $^3\Sigma_g^-$ )...M<sup>2+</sup> are also poorer than those of the C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>...M<sup>2+</sup> or B<sub>2</sub>H<sub>2</sub> ( $^1\Delta_g$ )...M<sup>2+</sup>. As can be seen from Table 2, at all levels, the binding energies follow the order HB=BH ( $^1\Delta_g$ )...M<sup>+</sup>/M<sup>2+</sup> >H<sub>2</sub>C=CH<sub>2</sub>...M<sup>+</sup>/M<sup>2+</sup>>HC≡CH...M<sup>+</sup>/M<sup>2+</sup>>

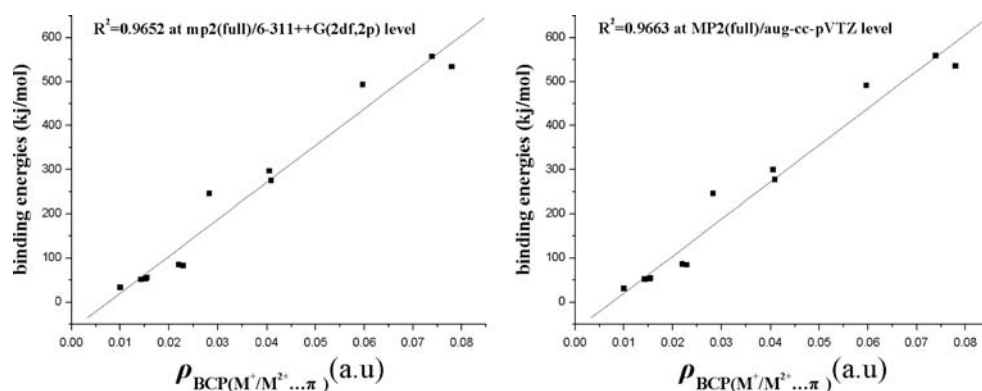
HB=BH ( $^3\Sigma_g^-$ )...M<sup>+</sup>/M<sup>2+</sup>. For example, the cation– $\pi$  interaction is 706.13, 556.94 or 533.78 kJ mol<sup>-1</sup> for HB=BH ( $^1\Delta_g$ )...Be<sup>2+</sup>, H<sub>2</sub>C=CH<sub>2</sub>...Be<sup>2+</sup> or HC≡CH...Be<sup>2+</sup>, whereas it is only 493.40 kJ mol<sup>-1</sup> for HB=BH ( $^3\Sigma_g^-$ )...Be<sup>2+</sup> at (U)MP2 (full)/aug-cc-pVTZ. So HB=BH ( $^3\Sigma_g^-$ ) can be viewed as a poorer  $\pi$ -electron donor in the cation– $\pi$  interaction compared to CC multiple-bond compounds, while HB=BH ( $^1\Delta_g$ ) is a stronger  $\pi$ -electron donor than CC multiple-bond monomers.

#### Vibration frequencies

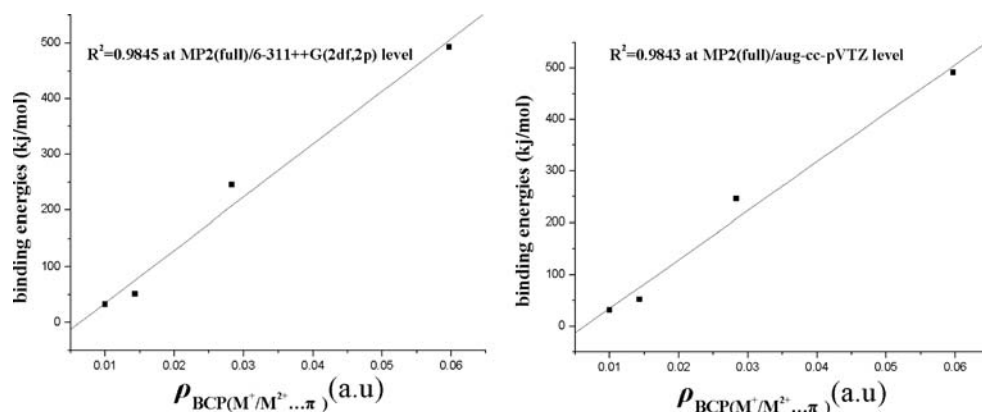
The larger the frequency shifts, the more stable the complex is; thus, we showed some important frequency shifts in order to investigate the relative stabilities of the complexes. The most important vibrational frequency of  $\pi$ -electron donor,  $\nu_1$ , can be described as stretching of the B=B bond. From Table 3 it can be seen that the  $\nu_1$  decreased (red shifts) and the IR intensity increased greatly in complexes compared to values obtained with the monomer HB=BH ( $^3\Sigma_g^-$ ), showing the formation of the cation– $\pi$  interaction. Except for HB=BH...H<sup>+</sup>, the complex HB=BH...Be<sup>2+</sup> is the most stable since it has the largest frequency shift (–199 cm<sup>-1</sup>), while HB=BH...Na<sup>+</sup> is the most unstable with the smallest frequency shift (only –24 cm<sup>-1</sup>), as is consistent with the analyses of geometries and binding energies.

The terms  $\nu_2$  and  $\nu_3$  can be approximately described as the anti-symmetrical stretching and symmetrical stretching frequencies of the B–H bond, respectively. From Table 3, although  $\nu_2$  decreased (red shifts) in the Be<sup>2+</sup> and Mg<sup>2+</sup> complexes and increased (blue shifts) in the other complexes, the frequencies changed most in HB=BH ( $^3\Sigma_g^-$ )...Be<sup>2+</sup> and least in HB=BH ( $^3\Sigma_g^-$ )...Na<sup>+</sup>. For  $\nu_3$ , the largest

**Fig. 2** The plot of binding energies versus  $\rho_{\text{BCP(cation}\dots\pi)}$



(a) The plot of binding energies versus  $\rho_{\text{BCP(cation}\dots\pi)}$  for all the complexes



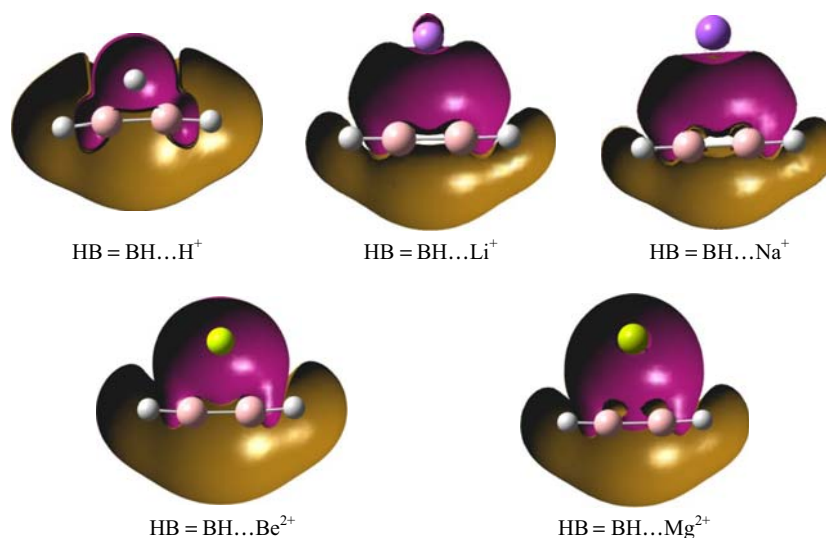
(b) The plot of binding energies versus  $\rho_{\text{BCP(cation}\dots\pi)}$  for the HB = BH complexes

shift was also found in HB=BH ( ${}^3\Sigma_g^-$ )...Be $^{2+}$ . These results show that the cation- $\pi$  interaction in HB=BH ( ${}^3\Sigma_g^-$ )...Be $^{2+}$  is the strongest, except for the H $^+$  complex, whereas it is weakest in HB=BH ( ${}^3\Sigma_g^-$ )...Na $^+$ , which is in accordance with the above analyses.

NBO analysis

To clarify the nature of the complexation, NBO analysis was carried out. From Table 4, we can see that, for the boron and carbon atoms, the NBO approach yields mainly

**Fig. 3** Shifts of electron density as a result of formation of the complex between cation and HB=BH ( ${}^3\Sigma_g^-$ ) (cutaway view). Purple regions denote gain, and yellow regions represent loss





only one kind of hybridization that involves the formation of cation– $\pi$  interactions. This hybridization is almost purely p (except for  $sp^{1.99}$  and  $sp^{1.23}$  in  $H_2C=CH_2 \dots H^+$  and  $HC\equiv CH \dots H^+$ , respectively) in character and is perpendicular to the molecular axis including the B=B or CC multiple bond to form the  $\pi$ -orbitals.

According to NBO analysis, all the complexes have two units, which is in agreement with the character of most interaction systems. In this study, delocalization effects between these two units can be identified from the presence of off-diagonal elements of the Fock matrix in the NBO basis, and the strengths of these delocalization interactions,  $E^{(2)}$  [42], can be estimated by second-order perturbation theory. From the results of  $E^{(2)}$ , we can see that the major interaction (except for the  $H^+$  complex) is that the B=B or CC multiple bond offers the  $p^{1.00}$ -hybridization  $\pi$ -electrons of the boron or carbon atoms to the contacting  $n^*$  antibonding orbital of the cation. Thus, the cation– $\pi$  interactions in these complexes are confirmed.

As can be seen from Table 4, for the  $HB=BH$  ( $^3\Sigma_g^-$ ) complexes of  $Be^{2+}$ ,  $Mg^{2+}$ ,  $Li^+$  and  $Na^+$ , the delocalization interactions  $E^{(2)}$  ( $\pi_{B=B} \rightarrow n^*_{\text{cation}}$ ) have stabilized the systems by 684.13, 413.22, 45.79 and 28.52  $\text{kJ mol}^{-1}$ , respectively. Since the  $E^{(2)}$  values follow the order  $HB=BH \dots Be^{2+} > HB=BH \dots Mg^{2+} > HB=BH \dots Li^+ > HB=BH \dots Na^+$ , the orders of the binding energy and stability are found to be  $HB=BH \dots Be^{2+} > HB=BH \dots Mg^{2+} > HB=BH \dots Li^+ > HB=BH \dots Na^+$ . On the other hand, the net charge transfer is evaluated to be from  $HB=BH$  to the cation by 342.2, 256.8, 26.5 and 18.9 me for the  $Be^{2+}$ ,  $Mg^{2+}$ ,  $Li^+$  and  $Na^+$  complexes, respectively. This indicates that the smaller cation with the greater charge allows the cation to more effectively withdraw electron density from the  $\pi$ -system, increasing the charge transfer and the covalent nature of the cation– $\pi$  interaction. Thus, the order of the binding energies is also suggested to be  $HB=BH \dots Be^{2+} > HB=BH \dots Mg^{2+} > HB=BH \dots Li^+ > HB=BH \dots Na^+$ . This result is in accordance with the geometries and analyses of the binding energies as well as our investigation into the cation– $\pi$  interaction between the singlet state  $HB=BH$  and the cation [1].

In  $H_2C=CH_2 \dots M^+/M^{2+}$  and  $HC\equiv CH \dots M^+/M^{2+}$ , we also noted the fact that the values of  $E^{(2)}$  in the  $Be^{2+}$  and  $Mg^{2+}$  complexes are significantly greater than those in the  $Li^+$  and  $Na^+$  complexes, suggesting that the cation– $\pi$  interactions in  $H_2C=CH_2 \dots M^{2+}$  and  $HC\equiv CH \dots M^{2+}$  are greater. Furthermore, the net charge transfer is evaluated to be from the CC multiple bonds to the cation by 326.1, 180.8, 28.8 and 19.4 me for  $H_2C=CH_2 \dots Be^{2+}$ ,  $H_2C=CH_2 \dots Mg^{2+}$ ,  $H_2C=CH_2 \dots Li^+$  and  $H_2C=CH_2 \dots Na^+$ , and 196.1, 109.8, 18.7 and 9.4 me for the corresponding  $HC\equiv CH$  complexes, respectively, indicating that the net charge transfer in the  $M^{2+}$  complexes is also stronger. In other words, the B=B or CC multiple bond can release more  $\pi$ -electrons toward  $M^{2+}$

than towards  $M^+$ . This is perhaps the origin of the stronger interaction in  $M^{2+}$  complexes than those in  $M^+$  complexes.

It is noteworthy that, although the values of  $E^{(2)}$  in the  $H^+$  complexes are weaker than those in the other complexes, perhaps due to the poorer electron-delocalization of  $sp^{1.99}$  and  $sp^{1.23}$  than with purely p hybridization to the cation, significantly greater net charge transfers are found in the  $H^+$  complexes (687.2 and 663.0 me) compared to those in other complexes. Such a remarkable net charge transfer suggests covalent interactions in the  $H^+$  complexes, as is also observed in most of cation– $\pi$  systems of  $H^+$  [1, 16].

#### AIM analysis

It is well known that knowledge of electronic characteristics is essential to revealing the nature of cation– $\pi$  interactions. As an advanced method, Bader's AIM method has been applied widely to study cation– $\pi$  interactions [44].

Our calculated AIM results show that, for each  $M^+/M^{2+} \dots \pi$  contact, there is a bond path linking the cation with the midpoint of the B=B or CC multiple bond accompanied by a BCP (see Fig. 1). Except for the  $H^+$  complex, the values of the electron densities  $\rho_{\text{BCP}(H \dots \pi)}$  obtained are within a range of 0.0100 – 0.0739 a.u. (see Table 5), and their Laplacian  $\nabla^2 \rho_{\text{BCP}}$  values are all positive, indicating the typical closed-shell type of interaction in the complexes. In other words, for these  $M^+/M^{2+} \dots \pi$  contacts, the small  $\rho_{\text{BCP}}$  and positive  $\nabla^2 \rho_{\text{BCP}}$  values are basically similar to the topological properties of normal  $M^+/M^{2+} \dots \pi$  bonds [44]. This result suggests the formation of cation– $\pi$  interactions and confirms that, akin to the CC multiple bond, the electron-deficient B=B double bond of  $HB=BH$  ( $^3\Sigma_g^-$ ) can also act as a  $\pi$ -electron donors to form cation– $\pi$  interactions.

In contrast, at the BCP of the  $H^+$  complex, the higher densities [0.1587, 0.1980 and 0.2155 a.u. for the  $HB=BH$  ( $^3\Sigma_g^-$ ),  $H_2C=CH_2$  and  $HC\equiv CH$ , respectively] and negative Laplacian values (–0.1386, –0.3000 and –0.3755) are indicative of covalent interaction, in accordance with our studies on the complex of the singlet state  $HB=BH$  with  $H^+$  [1]. In fact, in their investigation into  $H^+$  complexes with  $\pi$ -systems, Mohajeri and Karimi found that the densities are 0.19 – 0.27 a.u. at the BCP of complexes, and confirmed that negative Laplacian density values are indicative of covalent interaction [16].

From Tables 2 and 5, except for the  $H^+$  complex, the  $Be^{2+}$  complex has the highest electron density  $\rho_{\text{BCP}(\text{cation} \dots \pi)}$ , with the greatest binding energies in each kind of complex; in contrast, the  $Na^+$  with  $HB=BH$  ( $^3\Sigma_g^-$ ) or CC multiple-bond system has the least  $\rho_{\text{BCP}(\text{cation} \dots \pi)}$  with the poorest binding energy. Interestingly, a good linear relationship is observed between the binding energies and the electron densities  $\rho_{\text{BCP}(\text{cation} \dots \pi)}$ , and the correlation coefficient,  $R^2$ , is equal to 0.9652 and 0.9663 for all the complexes at MP2(full)/6–

311++G(2df,2p) and MP2(full)/aug-cc-PVTZ levels, respectively (see Fig. 2). For HB=BH ( $^3\Sigma_g^-$ ) complexes with cations, it is up to 0.9845 and 0.9843, respectively.

Additionally, the poorer cation– $\pi$  interactions in HB=BH ( $^3\Sigma_g^-$ )... $M^+/M^{2+}$  complexes compared to those in the  $H_2C=CH_2$  or  $HC\equiv CH$  complexes are also observed from the lower  $\rho_{BCPs(cation\cdots\pi)}$  in the former compared to those in the latter. For example, the values of  $\rho_{BCPs(cation\cdots\pi)}$  are 0.0739 and 0.0780 a.u. for the  $Be^{2+}$  complexes with  $H_2C=CH_2$  and  $HC\equiv CH$ , respectively, but only up to 0.0597 a.u. for HB=BH... $Be^{2+}$ .

#### Analysis of the electron density shifts

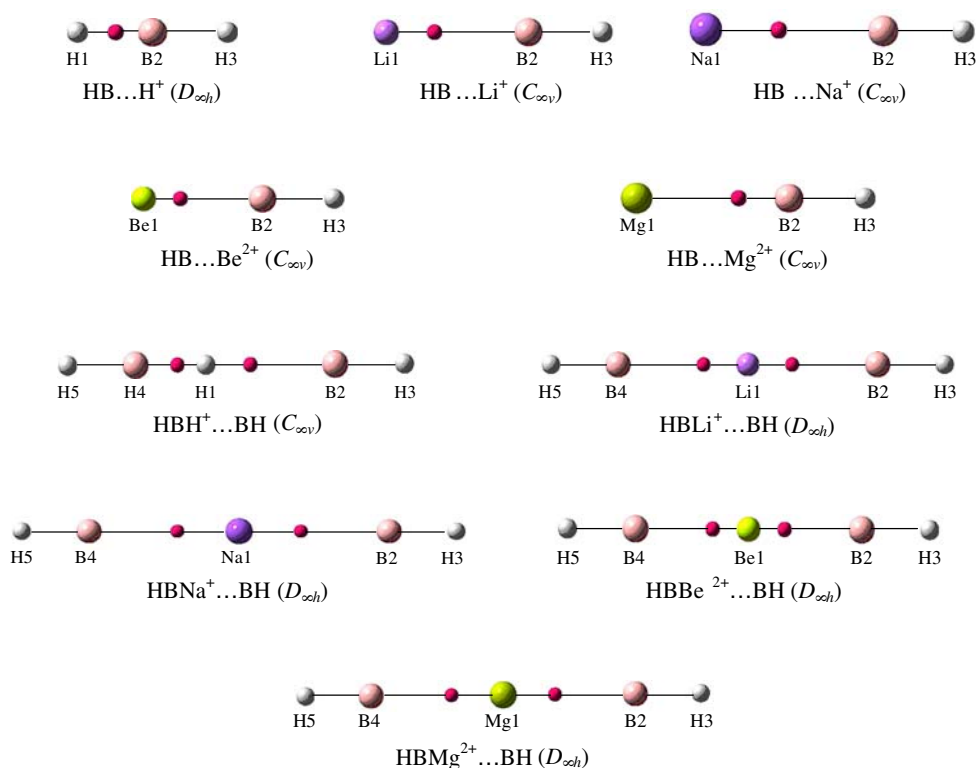
It is known that changes in the electron density distribution in both donors and acceptors are the most important consequence of the formation of the cation– $\pi$  interaction [48]. In order to obtain a deeper insight into the origin of the cation– $\pi$  interaction between the electron-deficient B=B bond of HB=BH ( $^3\Sigma_g^-$ ) and the cation, an analysis of the electron density shifts that accompany formation of the cation– $\pi$  interaction was carried out. The shifts of electron densities are illustrated in Fig. 3. Purple regions represent the accumulation of additional electron density as a result of the mutual approach of the two molecules; yellow regions indicate loss of density.

From Fig. 3, the most obvious effect of the cation– $\pi$  interaction is shown by the purple regions near the cation,

showing that the cation gains density. It can be noted that, for the  $H^+$  complex, the proton falls into the bottom of the purple region near the boron atoms, while for the other complexes cations are in the middle (for the  $Be^{2+}$  and  $Mg^{2+}$  complexes) or top (for the  $Li^+$  and  $Na^+$  complexes) of the purple region. This result shows that, for the  $H^+$  complex, the lost density of the B=B bonds has been concentrated in the internuclear region (valence region) between the proton and the two boron atoms, and the valence shell charge concentration of the two species forms one continuous region of charge concentration. Thus, a shared interaction in the  $H^+$  complex is confirmed, in accordance with the binding energies and investigation into the cation– $\pi$  interaction between  $H^+$  and  $H_2C=CH_2$ ,  $HC\equiv CH$  or HB=BH ( $^1\Delta_g$ ) [1, 16]. For the  $Be^{2+}$  or  $Mg^{2+}$  complex, the valence shell charge concentration is less than that in the  $H^+$  complex, suggesting that the poorer covalent properties of the cation– $\pi$  interaction in the  $Be^{2+}$  or  $Mg^{2+}$  complexes compared to that in the  $H^+$  complex with the  $\pi$  system. However, in the  $Li^+$  and  $Na^+$  complexes, the lost densities of the B=B bonds are concentrated in the middle of the regions between the cations and boron atoms, and the electron densities are confined separately to each interacting species, reflecting the closed-shell interaction.

Another effect is seen in the region along the B=B bond. For each of the cation– $\pi$  complexes, it is apparent from the notable yellow region around the B=B bond axis that there is much charge loss from the B=B bond, in accordance with

**Fig. 4** Molecular structures and BCPs of the cation– $\pi$  complexes HB=BH ( $^3\Sigma_g^-$ )/( $^1\Delta_g$ )... $M^+/M^{2+}$ ,  $H_2C=CH_2$ ... $M^+/M^{2+}$  and  $HC\equiv CH$ ... $M^+/M^{2+}$ . Small red spheres (unlabeled) represent bonds



**Table 6** Principal geometry parameters (in Å) and bond critical point (BCP) properties (in a.u.) for the  $\sigma$ -binding 1:1 and 2:1 complexes between BH and the cations at B3LYP/6–311++G(2df,2p) level

	HB...H <sup>+</sup>	HB...Li <sup>+</sup>	HB...Na <sup>+</sup>	HB...Be <sup>2+</sup>	HB...Mg <sup>2+</sup>
R(M <sup>+</sup> /M <sup>2+</sup> ...B)	1.173	2.286	2.645	1.964	2.369
$\rho_{\text{BCP}}(\text{M}^+/\text{M}^{2+} \dots \text{B})$	0.2269	0.0262	0.0196	0.0797	0.0424
$\nabla^2 \rho_{\text{BCP}}(\text{M}^+/\text{M}^{2+} \dots \text{B})$	−0.9165	0.0892	0.0684	0.0342	0.1000
	HBH <sup>+</sup> ...BH	HBLi <sup>+</sup> ...BH	HBNa <sup>+</sup> ...BH	HBBe <sup>2+</sup> ...BH	HBMg <sup>2+</sup> ...BH
R(M <sup>+</sup> /M <sup>2+</sup> ...B)	2.248 (1.225) <sup>a</sup>	2.316	2.680	1.959	2.386
$\rho_{\text{BCP}}(\text{M}^+/\text{M}^{2+} \dots \text{B})$	0.0262 (0.2104) <sup>a</sup>	0.0241	0.0181	0.0765	0.0400
$\nabla^2 \rho_{\text{BCP}}(\text{M}^+/\text{M}^{2+} \dots \text{B})$	0.0323 (−0.7744) <sup>a</sup>	0.0803	0.0631	0.0283	0.1016

<sup>a</sup> Values in parentheses are the distance and BCP properties of H<sup>+</sup>...B bond in HBH<sup>+</sup> moiety

the accepted notion that, due to the relative stronger fluidity of  $\pi$ -electrons, the  $\pi$ -orbital of B=B bond tends to lose density. Thus, it is confirmed that the electron-deficient B=B double bond of HB=BH ( $^3\Sigma_g^-$ ) can also act as a  $\pi$ -electron donor to form cation– $\pi$  interactions. The loss of density weakens the B=B bond, leading to its elongation and a decrease in strength, in agreement with geometrical analysis. Moreover, the yellow region in the Na<sup>+</sup> complex is the smallest, indicating that the charge loss of the B=B bond in the Na<sup>+</sup> complex is the least, with the poorest cation– $\pi$  interaction, in agreement with the above analyses.

Therefore, we can conclude that the nature of the cation– $\pi$  interaction is that many of the lost densities from the  $\pi$ -orbital of the B=B bond are shifted toward the cations, leading to accumulation of electron density and the formation of the cation– $\pi$  interaction. Furthermore, it is obvious from the electron density shifts that the H<sup>+</sup> complex is indicative of covalent interaction, and the Be<sup>2+</sup> or Mg<sup>2+</sup> complexes have poorer covalent properties of cation– $\pi$  interaction than that of the H<sup>+</sup> complex.

A comparison with the  $\sigma$ -binding complex

#### Geometry of the complex

The atomic labels and BCPs of the  $\sigma$ -binding 1:1 and 2:1 complexes between BH and the cations are shown in Fig. 4, and the geometry parameters and binding energies are listed in Tables 6 and 7, respectively. Except for HB...H<sup>+</sup> ( $D_{\text{oh}}$ ), the 1:1 complexes are of  $C_{\infty v}$  symmetry. In the 2:1 complexes, HBM<sup>+</sup>/M<sup>2+</sup>...BH, HBH<sup>+</sup>...BH has  $C_{\infty v}$  symmetry, while the others form  $D_{\text{oh}}$  shapes.

As can be seen from Table 6, the distances of the M<sup>+</sup>/M<sup>2+</sup>...B bonds in the  $\sigma$ -binding Li<sup>+</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> complexes are less than those of the M<sup>+</sup>/M<sup>2+</sup>... $\pi$  bonds in the corresponding cation– $\pi$  complexes. For example, the distances of Li<sup>+</sup>...B bonds in HB...Li<sup>+</sup> and HBLi<sup>+</sup>...BH are 2.286 and 2.316 Å, whereas the corresponding values of the Li<sup>+</sup>... $\pi$  bonds in HB=BH ( $^3\Sigma_g^-$ )...Li<sup>+</sup> and HB=BH ( $^1\Delta_g$ )...Li<sup>+</sup> are 2.475 and 2.486 Å at (U) B3LYP/6–311++G(2df,2p) level, respectively. For the  $\sigma$ -binding Be<sup>2+</sup> complexes, the distances of the Be<sup>2+</sup>...

**Table 7** Binding energies of the  $\sigma$ -binding 1:1 and 2:1 complexes between BH and the cations at B3LYP/6–311++G(2df,2p) level [ $-D_e$  (kJ mol<sup>−1</sup>)]

HB...H <sup>+</sup>	HB...Li <sup>+</sup>	HB...Na <sup>+</sup>	HB...Be <sup>2+</sup>	HB...Mg <sup>2+</sup>
894.03 <sup>a</sup> 862.51 <sup>c</sup>	152.40 <sup>a</sup> (151.63) <sup>b</sup> 140.42 <sup>c</sup>	112.00 (110.17) 100.79	703.81 (703.17) 688.83	427.51 (426.16) 414.01
HBH <sup>+</sup> ...BH	HBLi <sup>+</sup> ...BH	HBNa <sup>+</sup> ...BH	HBBe <sup>2+</sup> ...BH	HBMg <sup>2+</sup> ...BH
−50.96203 <sup>d</sup> −51.02393 <sup>c</sup>	−57.98697 −58.09420	−212.76260 −212.88947	−64.71640 −64.64264	−250.12630 −250.13691
−51.07831 <sup>f</sup>	−58.08541	−212.87577	−64.69116	−250.16835
69.26 (68.08) 51.00	126.24 (124.92) 100.30	94.94 (92.65) 70.05	525.74 (524.60) 493.90	333.83 (331.89) 304.68

<sup>a</sup> Uncorrected binding energies

<sup>b</sup> BSSE-corrected binding energies [ $-D_{e(\text{BSSE})}$ ]

<sup>c</sup> Binding energies with BSSE and ZPE [ $-D_{e(\text{BSSE-ZPE})}$ ] correction

<sup>d</sup> Total energies of HBM<sup>+</sup>/M<sup>2+</sup>...BH

<sup>e</sup> Total energies of HB=BH( $^3\Sigma_g^-$ )...M<sup>+</sup>/M<sup>2+</sup>

<sup>f</sup> Total energies of HB=BH( $^1\Delta_g$ )...M<sup>+</sup>/M<sup>2+</sup>

B bonds in the 1:1 and 2:1 complexes are larger than that of the  $\text{Be}^{2+}\dots\pi$  bond in  $\text{HB}=\text{BH} (^3\Sigma_g^-)\dots\text{Be}^{2+}$  but lower than that in  $\text{HB}=\text{BH} (^1\Delta_g)\dots\text{Be}^{2+}$ .

It is noteworthy that, in the  $\sigma$ -binding  $\text{HBH}^+\dots\text{BH} (C_{\infty v})$  complex, the distances of  $\text{H}^+\dots\text{B}$  bonds are 1.225 and 2.248 Å, respectively. For both of the  $\text{H}^+\dots\text{B}$  bonds, one is close to those of  $\text{H}^+\dots\pi$  bonds in the cation– $\pi$  complexes  $\text{HB}=\text{BH}\dots\text{H}^+$ , and such a short  $\text{H}^+\dots\text{B}$  bond indicates that one of the  $\sigma$ -binding  $\text{H}^+\dots\text{B}$  interactions in  $\text{HBH}^+\dots\text{BH}$  behaves covalently. However, the length of the other  $\sigma$ -binding  $\text{H}^+\dots\text{B}$  bond in  $\text{HBH}^+\dots\text{BH}$  is much greater than that of the covalent character  $\text{H}^+\dots\text{B}$  or  $\text{H}^+\dots\pi$  bond in  $\text{HB}=\text{BH}\dots\text{H}^+$ , suggesting a weak interaction, in agreement with our AIM analyses of  $\text{HBH}^+\dots\text{BH}$ . For  $\text{HBH}^+\dots\text{BH}$ , one of the values of the Laplacians  $\nabla^2\rho_{\text{BCP}(\text{H}\dots\text{B})}$  is positive (0.0323), while the other is negative (−0.7744; see Table 6).

### Binding energies and stabilities

From Table 7, the  $\sigma$ -binding energies obtained from B3LYP/6–311++G(2df,2p) level follow the same order of  $\text{HB}\dots\text{H}^+>\text{HB}\dots\text{Be}^{2+}>\text{HB}\dots\text{Mg}^{2+}>\text{HB}\dots\text{Li}^+>\text{HB}\dots\text{Na}^+$ , as is similar to the sequence of the cation– $\pi$  interactions between  $\text{HB}=\text{BH} (^1\Delta_g)$  or  $\text{HB}=\text{BH} (^3\Sigma_g^-)$  and cations. However, except for  $\text{HB}\dots\text{H}^+$ , the  $\sigma$ -binding interaction energy of  $\text{HB}\dots\text{M}^+/\text{M}^{2+}$  is always markedly stronger than the cation– $\pi$  interaction energy of the  $\text{C}_2\text{H}_2\dots\text{M}^+/\text{M}^{2+}$ ,  $\text{C}_2\text{H}_4\dots\text{M}^+/\text{M}^{2+}$ ,  $\text{B}_2\text{H}_2 (^1\Delta_g)\dots\text{M}^+/\text{M}^{2+}$  or  $\text{B}_2\text{H}_2 (^3\Sigma_g^-)\dots\text{M}^+/\text{M}^{2+}$  complexes. For example, the interaction energy has been evaluated to be 151.63 kJ mol<sup>−1</sup> for  $\text{HB}\dots\text{Li}^+$  after correction of the BSSE at B3LYP/6–311++G(2df,2p) level, while it is only 91.00, 90.96, 119.55 and 56.33 kJ mol<sup>−1</sup> for  $\text{C}_2\text{H}_2\dots\text{Li}^+$ ,  $\text{C}_2\text{H}_4\dots\text{Li}^+$ ,  $\text{B}_2\text{H}_2 (^1\Delta_g)\dots\text{Li}^+$  and  $\text{B}_2\text{H}_2 (^3\Sigma_g^-)\dots\text{Li}^+$ , respectively.

We also calculated the total energies of  $2\text{BH}$  (−50.59700 a.u.),  $\text{B}_2\text{H}_2 (^1\Delta_g)$  (−50.75465 a.u.) and  $\text{B}_2\text{H}_2 (^3\Sigma_g^-)$  (−50.78754 a.u.) with the B3LYP/6–311++G(2df,2p) method. It was found that  $2\text{BH}$  is less stable than  $\text{B}_2\text{H}_2 (^1\Delta_g)$  and  $\text{B}_2\text{H}_2 (^3\Sigma_g^-)$  by 413.85 and 500.19 kJ mol<sup>−1</sup>, respectively. From Table 7 we have also observed that, except for  $\text{HBBe}^{2+}\dots\text{BH}$ , the 2:1  $\sigma$ -binding complexes between  $\text{BH}$  and the cations are also less stable than the cation– $\pi$  complexes of  $\text{B}_2\text{H}_2 (^1\Delta_g)$  or  $\text{B}_2\text{H}_2 (^3\Sigma_g^-)$ . For instance, the  $\sigma$ -binding  $\text{HBLi}^+\dots\text{BH}$  complex is higher in energy by 281.49 kJ mol<sup>−1</sup> for  $\text{B}_2\text{H}_2 (^3\Sigma_g^-)\dots\text{Li}$  and 258.41 kJ mol<sup>−1</sup> for  $\text{B}_2\text{H}_2 (^1\Delta_g)\dots\text{Li}$  at B3LYP/6–311++G(2df,2p) level, respectively.

For the 2:1 complexes, we defined the second  $\sigma$ -binding energies as follows:

$$D_e = E_{\text{complex}} - E_{(\text{HBM}^+/\text{M}^{2+})_{\text{mono}}} - E_{(\text{BH})_{\text{mono}}} \quad (3)$$

As can be seen from Tables 2 and 7, the  $\sigma$ -binding interaction energy of  $\text{HBLi}^+/\text{Na}\dots\text{BH}$  is stronger than the

corresponding cation– $\pi$  interaction in the  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{B}_2\text{H}_2 (^1\Delta_g)$  or  $\text{B}_2\text{H}_2 (^3\Sigma_g^-)$  complexes. However, the interaction energy of  $\text{HBBe}^{2+}\dots\text{BH}$  is less than that of  $\text{B}_2\text{H}_2 (^3\Sigma_g^-)\dots\text{Be}^{2+}$  and  $\text{B}_2\text{H}_2 (^1\Delta_g)\dots\text{Be}^{2+}$ , and weaker for  $\text{HBMg}^{2+}\dots\text{BH}$  than for  $\text{B}_2\text{H}_2 (^1\Delta_g)\dots\text{Mg}^{2+}$  but greater than that of  $\text{B}_2\text{H}_2 (^3\Sigma_g^-)\dots\text{Mg}^{2+}$ . In particular, we have found that the second  $\sigma$ -binding interaction energy of  $\text{HBH}^+\dots\text{BH}$  is only 69.26 kJ mol<sup>−1</sup>, obviously lower than the corresponding cation– $\pi$  interaction energy in the complex of the  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{B}_2\text{H}_2 (^1\Delta_g)$  or  $\text{B}_2\text{H}_2 (^3\Sigma_g^-)$ , indicating that it is not covalent binding but a weak interaction, in agreement with the structures and AIM analyses.

### Conclusions

We performed calculations using UMP2(full) and UB3LYP methods at 6–311++G(2df,2p) and aug-cc-pVTZ levels for the triplet state  $\text{HB}=\text{BH} (^3\Sigma_g^-)$  with  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$  systems. The nature of the unusual cation– $\pi$  interaction involving the electron-deficient  $\text{B}=\text{B}$  double bond was investigated. The interaction energies follow the order  $\text{HB}=\text{BH}\dots\text{H}^+>\text{HB}=\text{BH}\dots\text{Be}^{2+}>\text{HB}=\text{BH}\dots\text{Mg}^{2+}>\text{HB}=\text{BH}\dots\text{Li}^+>\text{HB}=\text{BH}\dots\text{Na}^+$ . Furthermore, the calculations show that the interaction energy of  $\text{HB}=\text{BH} (^3\Sigma_g^-)\dots\text{M}^+/\text{M}^{2+}$  is poorer than that between the corresponding cation and  $\text{HB}=\text{BH} (^1\Delta_g)$ ,  $\text{HC}\equiv\text{CH}$  or  $\text{H}_2\text{C}=\text{CH}_2$ , and, except for  $\text{HB}\dots\text{H}^+$ , the  $\sigma$ -binding interaction energy of  $\text{HB}\dots\text{M}^+/\text{M}^{2+}$  is always markedly stronger than the cation– $\pi$  interaction energy of the  $\text{C}_2\text{H}_2\dots\text{M}^+/\text{M}^{2+}$ ,  $\text{C}_2\text{H}_4\dots\text{M}^+/\text{M}^{2+}$ ,  $\text{B}_2\text{H}_2 (^1\Delta_g)\dots\text{M}^+/\text{M}^{2+}$  or  $\text{B}_2\text{H}_2 (^3\Sigma_g^-)\dots\text{M}^+/\text{M}^{2+}$  complexes. For the 2:1 complex  $\text{HBH}^+\dots\text{BH}$ , one of the  $\text{H}^+\dots\text{B}$  interactions indicates covalent character; the other indicates a weak interaction. The NBO, AIM theory and electron density shift analyses reveal that the nature of the cation– $\pi$  interaction between  $\text{HB}=\text{BH} (^3\Sigma_g^-)$  and  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Be}^{2+}$  or  $\text{Mg}^{2+}$  is that much of the density lost from the  $\pi$ -orbital of the  $\text{B}=\text{B}$  bond is shifted towards the cation. It is obvious from the electron density shifts that the  $\text{H}^+$  complex is indicative of covalent interaction, and that the cation– $\pi$  interaction the  $\text{Be}^{2+}$  or  $\text{Mg}^{2+}$  complex has poorer covalent properties than that in the  $\text{H}^+$  complex.

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